Morphological Control of Mesoscale Colloidal Models

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Abstract

Colloidal systems have proven useful mesoscale models because of their relatively large size, slow dynamics, and the ease with which one can alter the interactions between individual particles. Studies of these systems are often conducted by varying the effective pair potential and then studying the resulting morphologies through microscopy or scattering techniques. Using optical-based manipulation methods however, one can directly assemble colloidal morphologies of interest. By spatially modulating laser-light intensity with a single scanning laser, we have been able to create optical traps of arbitrary design and construct colloidal structures of very specific morphology. In addition, once trapped, we have been able to lock in these structures using polymerization techniques. Our goal is to use this approach to both help us understand fundamental thermodynamic processes and to create templates for morphologies which would not otherwise develop.

Introduction

Colloidal dispersions have proven to be very useful mesoscale models of molecules. In general, molecular level investigations are extremely difficult due to the small molecular sizes and the rapid time scales involved. Compared to molecular systems, colloids are relatively large, correspondingly slow, can be directly manipulated, and their interactions can be easily tuned [1]. For example, repulsions can be modified by changing solution ionic strength [2,3] and interparticle attractions that arise due to van der Waals forces can be influenced by index matching or salt concentration [4,5]. Because of the advantages inherent in using colloidal systems, we intend to use colloids as mesoscale models of molecules. Thermodynamic studies using these models are sometimes limited by the kinetics of structure formation however. Having the possibility to directly manipulate these models would provide the ability to bypass kinetic limitations and study colloidal structures of very specific design and morphology.

In 1970, Ashkin and coworkers [6] demonstrated the feasibility of trapping micron and submicron particles in solution with a single laser beam focused to a diffraction-limited spot. This novel experimental tool, named optical tweezers, has quickly become popular because laser-based optical traps can precisely position and manipulate microscale objects without physical contact. These optical manipulation techniques allow us to control our model systems in a direct fashion and construct morphologies of our design, including those in metastable, stable and unstable states.

Although rigorous theoretical description of optical tweezers is not trivial [7], the basic principle of laser traps can be understood in terms of the transfer of momentum carried by laser photons redirected by refraction while passing through a particle [8]. Because momentum is conserved, the momentum change in the deflected rays results in an equal and opposite momentum change of the colloid, producing a force via Newton's Second Law [9,10]. The net effect of all the laser rays impinging on a particle with high index of refraction is to push it towards the region of highest light intensity, i.e. the laser focal point, where the net force acting on the particle is zero.

The optical forces on trapped particles are usually divided into two types: the scattering and the gradient force. The former is proportional to the light intensity and is directed along the propagation light axis, the latter is proportional to and directed along the light-intensity gradient. Stable trapping is obtained when the gradient force is larger than the scattering force, i.e. with very steep light gradients, such as those obtainable with high-numerical aperture objectives that are able to produce a sharp laser focus [11]. Optical trapping, however, is not limited to particles with low absorption coefficient and index of refraction greater than that of the surrounding medium. In fact, using “optical cages” [12] or “optical vortices” [13], reflective, absorbing and low-refractive-index particles can be trapped as well.

Due to their sterile and non-intrusive nature, laser tweezers have found many applications in biology. Examples include the manipulation of bacteria [14], viruses [15], organelles [16] and DNA [17,18]. In chemistry and physics they have been used to measure colloidal

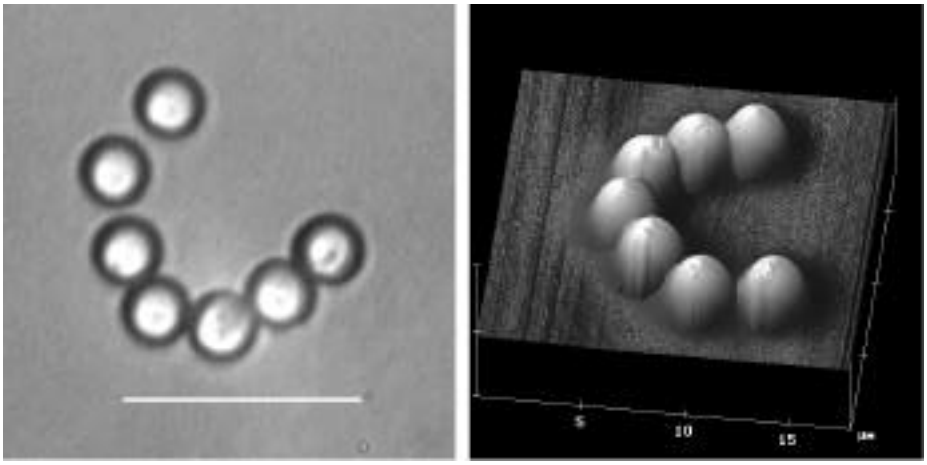
interactions, polymers and colloids dynamics and physical properties of membranes and vesicles (see [19] for a review). Recently, optical tweezers have also been employed to stick particles one by one on a substrate [20] and to image soft samples in solution by using the trapped particle as the probe of a novel type of scanning probe microscope [21].

The basic single-trap design has been modified in several ways to create multiple optical traps, thus allowing spatial orientation of asymmetric particles and manipulation of several objects or two parts of the same object simultaneously. Multiple traps can be obtained in different ways: for example, splitting a single laser beam with beamsplitters [22], using diffractive optics [23,24], or interference between two beams [25] to create light-intensity patterns in the sample. A recent approach relies on steering a single beam with galvanomirrors [26] along several points in the sample plane thus creating an effective light pattern. Because of its flexibility, we have used this last time-sharing technique to implement a scanning laser optical trap (SLOT) that uses fast piezoelectrics to move the beam and allows us to simultaneously manipulate several colloids and position them in any chosen pattern.

In our setup, the laser beam is moved in the sample plane by tilting a piezoelectric mirror along the optical path. The piezoelectric device can reach scanning rates up to 10^4 Hz allowing to retrap a particle before it escapes the optical well due to Brownian diffusion. The minimum required scan rate is inversely proportional to the medium viscosity and inversely proportional to the particle radius to the third power [27]. For example, scan rates of the order of 100 Hz must be used to trap micron-sized particles in water, while for

particles with radius of 100 nm, a scan rate around 10^4 Hz is necessary. Because of our use of piezoelectrics, we are able to manipulate small particles (down to 0.8 μm in diameter) in low-viscosity solvents, such as water.

After trapping colloids with SLOT, we have permanently frozen the particles in their position by photopolymerizing the surrounding solvent and then characterized the resulting structure via atomic-force microscopy (AFM) (figures 1 and 2). These permanent 2D patterns will be used to direct the crystallization of 3D colloidal structures. By changing the design or the particle spacing in the 2D colloidal pattern, 3D structures with different geometries can be induced. Colloidal crystals are receiving broad interest because they may find a wide variety of applications, including materials for photonics, lithograpy, or chemical sensors [28].



a b

Figure 1. Video (a) and AFM (b) images of 3-μm polystyrene particles after trapping and polymerization of the solvent ((a) scale bar: 10 μm; (b) height scale: 3.5 μm)

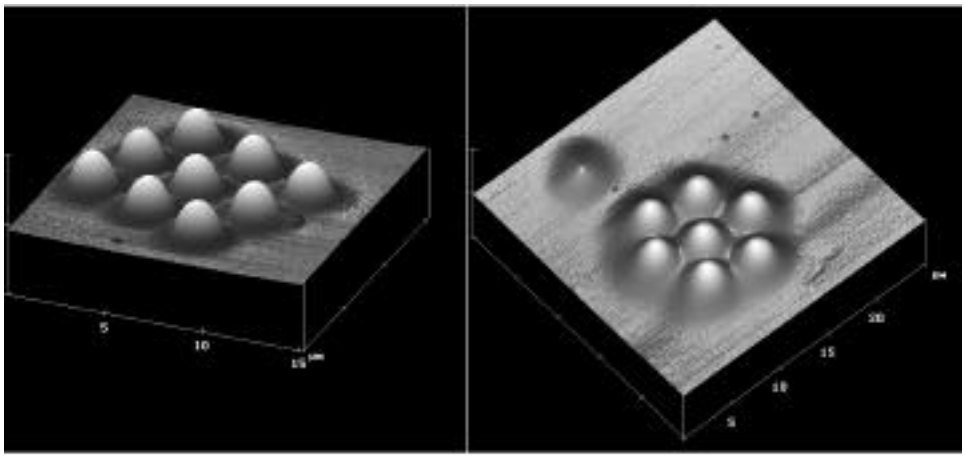


Figure 2. AFM image of 2.1-μm polystyrene particles after trapping and polymerization of the solvent (height scale: 2.2 μm)

Other researchers have built colloidal crystals relying on particle self-assembly based on the colloidal electrostatic interactions [29], by gentle centrifugation [30], or by sedimentation of colloidal particles from dilute dispersions [31,32]. Some modifications of these methods have involved steady shear conditions [33,34], ultrasonication [35], oscillatory shear [36], and the use of temperature gradients to start the nucleation and growth of the crystals [37]. In all these approaches, however, the degree of control over the final 3D structure is minimal. Recently, van Blaaderen and coworkers [38] have performed crystallization from settling dispersions driven by colloidal epitaxy. They used electron-beam lithography to etch holes in a layer of polymethylmethacrylate. Slow sedimentation of silica particles in these holes produced a first layer of microspheres that acted as a

template for subsequent colloidal crystal growth. They were thus able to control the lattice structure and the orientation of the 3D crystals, albeit into very specific morphology.

Experimental Setup

In our experiment, the laser is first expanded by a lens of focal length = 250 mm, hits a mirror set at 45 degrees and attached to a piezo tilt platform (model S-315.10, Physik Instrumente, Waldbronn, Germany), goes through two lenses (focal lengths 250 mm and 88.3 mm), and is finally focused in the sample plane by an oil-immersion objective with NA = 1.3 and focal lengh = 1.82 mm (CFN plan fluor 100x, Nikon, Melville, NY, USA). The distances between the optical elements along the beam path are set so that four conditions are met [39]:

1) the piezoelectric mirror and the objective back aperture are conjugate;
2) the size of the scanned area in the sample is approximately 20 x 20 μm^2;
3) the objective back aperture is overfilled with the laser beam;
4) the beam diverges at 160 mm from the objective thus achieving the sharpest possible laser focus, i.e. maximum trapping force.

The piezoelectric positioner has a maximum tilt angle of 1.2 mrad and is controlled by a Macintosh computer, a data acquisition board (PCI-MIO-16E-4, National Instruments, Austin, TX, USA) and software written in Labview (Labview 5.0, National Instruments, Austin, TX, USA). The laser is a CW 532-nm frequency-doubled diode-pumped Nd:YVO_4

solid-state laser (Millenia V, Spectra Physics, Mountain View, CA, USA) with Gaussian beam (TEM_{00} mode) of diameter 2.5 mm and power adjustable from 0.2 to 5 W. The trapping experiment is monitored with a monochrome videocamera (Sony XC-75, Edmund Scientific, Barrington, NJ, USA) placed on top of the microscope (Optiphot 150, Nikon, Melville, NY, USA).

Figures 3 and 4 show some multiple-particle arrangements of 1.5-μm silica particles (Bangs Laboratories, Inc., Fishers, IN, USA) in water. The laser power was set at around 0.6 W and the scanning frequency at 350-600 Hz.

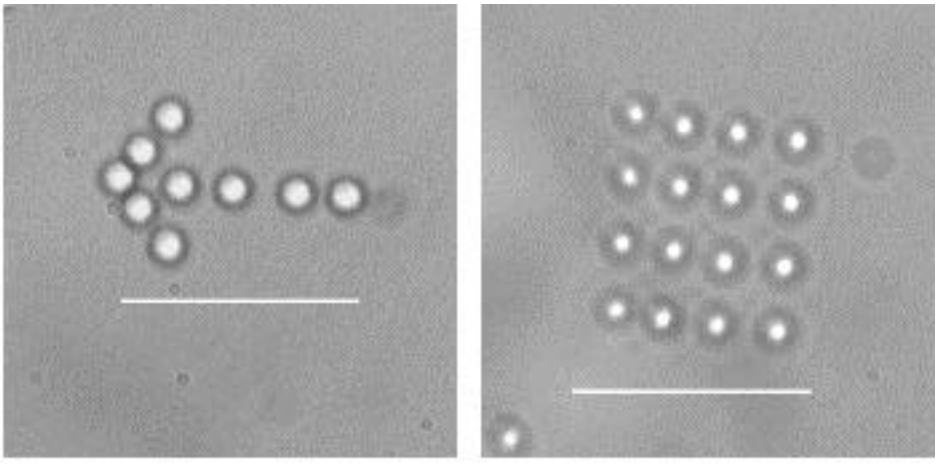


Figure 3. 1.5-μm silica particles trapped in water using SLOT (scale bars: 10 μm)

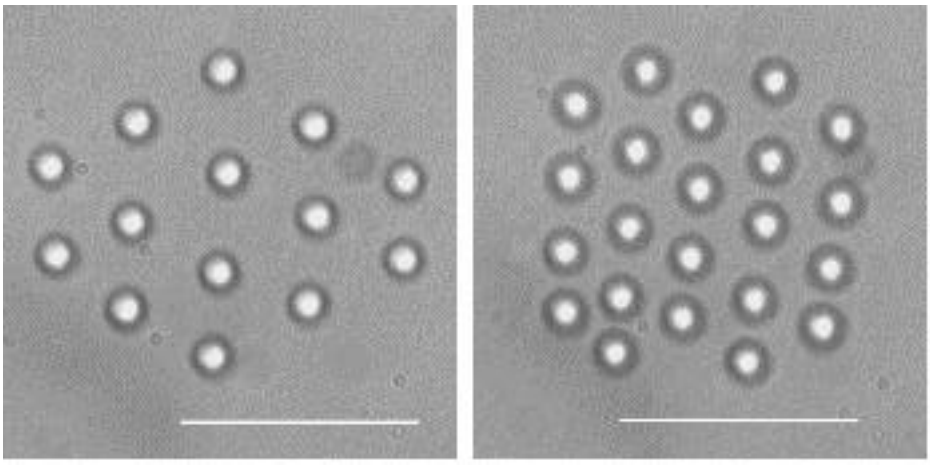


Figure 4. 1.5-μm silica particles trapped in water using SLOT (scale bars: 10 μm)

Experimental Procedure

We built permanent colloidal structures by trapping the particles in a desired pattern and then polymerizing the surrounding medium thus locking the particles in their trapped positions. The suspension solvent was an aqueous solution of acrylamide (1.56 M, 99 + %, Aldrich, Milwaukee, WI, USA), methylene-bis-acrylamide (0.038 M, 99 %, Aldrich, Milwaukee, WI, USA) and 2-hydroxy-2-metyl-1-phenyl-1-propanone as photoinitiator (Darocur 1173, 0.2 M, 95 %, Ciba Specialty Chemicals, Tarrytown, NY, USA).

First, a drop of colloidal suspension is placed on a microscope slide and covered with a standard cover slip. The microscope slide has been previously treated with an octadecyl

silicone coating (Glass Clad 18, United Chemical Technologies, Inc., Bristol, PA, USA) to make the glass surface hydrophobic thus facilitating successive removal of the polymerized matrix. The laser beam is then turned on and the particles are trapped in the desired design. The optics are arranged along the path such that particles are trapped close to the bottom of the sample cell.

Photopolymerization of the solvent is initiated using a UV lamp (S-363 Sperti Sunlamp, Cooper Hewitt Electric Corporation, Enangler, KY, USA). The UV light is focused in the sample plane from the bottom of the microscope by the same condenser used for the microscope illumination. Photopolymerization of the monomer-containing solution is very fast: after 5-10 seconds the trapping beam can be turned off without the particles diffusing away. The locked-in structures are characterized using tapping mode AFM (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA, USA). Figure 1 shows 3-μm polystyrene particles (Interfacial Dynamics Corporation, Portland, OR, USA) in a "C" pattern . Figure 2 shows the AFM images of 2.1-μm polystyrene particles (Interfacial Dynamics Corporation, Portland, OR, USA) after trapping and polymerization of the medium.

Discussion and Conclusions

We have implemented a technique to manipulate colloidal models where multiple particles (1.5 to 3 μm in diameter) can be set in a chosen pattern. The colloids are positioned using a scanning-laser optical trap technique that allows simultaneous manipulation of many micro-

objects in solution. This is achieved by rapidly steering a well-focused laser beam in the sample by tilting a fast piezoelectric mirror.

Following particle trapping, the colloids can be frozen in place by photopolymerization of the monomer-containing solvent. These 2D colloidal structures may find application as lithographic masks, diffraction gratings or as seeds for 3D crystallization of colloidal structures that could be used as photonic materials or biological/chemical sensors [40]. We will use the 2D colloidal surfaces to induce the formation of 3D colloidal structures by settling microparticles on top of the previously made 2D patterns. By changing the design and the particle spacing in the 2D structures, we will investigate the possibility of constructing different geometries in the growing 3D arrays. In this way we will be able to direct the formation of the final crystalline structure, instead of solely relying on particle self-assembly. This seeded crystal growth will be useful in fundamental studies on heterogeneous crystallization.

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